A credible alternative to the WPA process

This paper by **Dr. Joseph A. Megy** outlines the economic, environmental, and quality advantages of the Improved Hard Process over the wet acid process for the manufacture of phosphoric acid.

About the author

Dr. Joseph A Megy is the principle of JDC, Inc. He received a BSc (Mathematics, Chemistry Minor) degree in 1967 and a PhD (Chemistry and Chemical Engineering) in 1975 from Oregon State University. In 1978, he completed the Advanced Studies Program at MIT in Materials Engineering and R&D management, and then joined the corporate research staff of Occidental Petroleum at Irvine, California. During 1978, he was a group leader, and between 1979-83 director of pyrometallurgical engineering. Two major projects, including the KPA process, were developed to the pilot plant stage under his direction. Dr. Megy started CM Tech, Inc. in 1988. During the next 12 years he developed production plants in West Virginia and Missouri producing potassium titanium fluoride and titanium/zirconium additives used in the aluminum industry. Dr. Megy was SBA Small Businessman of the Year and his companies twice won the Governors Award for exporting excellence. All three of his products became dominant in their markets. All of the processes were invented and developed by Dr. Megy, who holds over 20 US patents and a number of foreign patents on metallurgical processes. In 1996, Dr. Megy started JDC, Inc., which is an R&D company primarily for development of processes related to Dr. Megy's manufacturing plants. In 2001, Dr. Megy turned over the direct operations of his companies to a president in order to focus on the activities of JDC, Inc.

The wet acid process has been used to produce phosphoric acid from phosphate ore and sulphuric acid commercially since approximately 1842. The process yields an impure, black phosphoric acid solution with about 26% P_2O_5, which is concentrated to make solid fertilizers (DAP and MAP) or purified to make liquid fertilizers or super phosphoric acid (SPA). The solution can also be further purified to make a technical-grade acid for various industrial markets. Except for a period during the last century, when the electric furnace acid process produced nearly as much phosphoric acid as the wet acid process, it has been the dominant manufacturing method for producing phosphoric acid. However, it does require highly beneficiated ores as a raw material, makes a rather weak and impure grade of phosphoric acid, and has a negative environmental footprint.

In 1981, Dr. Robert Hard, who was working for Occidental Research Corporation (ORC), made an important discovery that opened the door for a long-sought, efficient, high-temperature, kiln-based process to convert agglomerated mixtures of petroleum coke, low-grade phosphate ore, and silica into high-purity phosphoric acid for the $20 billion dollar world market.[1] ORC tested the Hard Process in two continuous pilot kiln tests in December 1981 and May 1982.[2, 3] High-purity phosphoric acid was made during these tests, with yields of over 70% in a commercial operating mode, and over 80% in a test mode. However, the operating window was small, throughput was less than commercially desired, and operating parameters were not optimised. The ORC laboratory closed down in 1982 for reasons unrelated to the development of the Hard Process. Although the biggest hurdle for the development of the Kiln Phosphoric Acid (KPA) process (e.g. melting of the kiln burden) had been overcome, it was still not ready for commercialisation.

Partially funded by two grants from the US Department of Agriculture (USDA), Jamegy Development Corporation (JDC) reactivated a KPA research programme, conducted principally at the Pacific Northwest National Laboratory and a development programme conducted at JDC facilities and vendor laboratories. Over the past four years, several important discoveries have been made that resulted in the modification of the Hard Process. These deliver high yields, high throughputs, optimised operating parameters and a broad, stable operating range.[4, 5] This work included engineering studies that evaluated the 2004 operating and capital cost of a commercial Improved Hard Process facility. The new discoveries have resulted in process modifications that are included in a recently-allowed patent.[6]

The Improved Hard Process will permit the use of leaner phosphate ores because it has greater tolerance of some common impurities, such as silica, organic content and magnesium. It will also reduce the environmental impact of gypsum stacks because an inert solid aggregate is the by-product of the process, not gypsum. This process produces superphosphoric (SPA)-grade acid at a significantly reduced cost compared with the wet acid process. Higher grade acid can be more efficiently utilised by the fertilizer industry and other end-users.

This paper quantifies these advantages when the process is used with ore from the Southern Extension of the Central Florida phosphate deposit, the North Carolina phosphate deposit, and the Idaho deposits

of the Meade Formation – three diverse ores that are important to the US phosphate fertilizer industry. Together they supply the majority of the current US phosphoric acid production plants. The following three analyses each consider a facility containing one large kiln producing 200,000 t/a of phosphoric acid of SPA grade (76% P_2O_5) suitable for the manufacture of liquid fertilizers. The facilities are evaluated for operating costs in 2004.

History

The high-temperature reaction of agglomerated phosphate ore, silica and carbonaceous material produces phosphorus metal and carbon monoxide gaseous products. When the P and CO off-gases from this reaction are burned with air, enough heat is released to supply all the heat necessary for an efficient thermal phosphoric acid production process. Methods attempting to utilise this source of heat in a thermal phosphoric acid production process are nearly 100 years old. The blast furnace concept led to the development of two commercial plants in the 1920s.[7] Although these furnaces produced a high quality phosphoric acid product and used no electricity for resistance heating, they required about five times theoretical carbon, because of a low level of heat integration, and involved large, recirculated gas flows. As a result, the blast furnaces were marginally more expensive than the electric furnace process that uses electricity to supply the heat for the reduction reaction, and discards the heat developed in burning the phosphorus metal and carbon monoxide.[8]

Between 1937 and 1983, highly integrated processes based on a rotary kiln reactor, collectively called the KPA process, have been advanced by a number of researchers.[9-15] These processes failed commercially because of a combination of burden melting and operating problems. However, researchers realised that if electric resistance heating could be replaced in an electric furnace process by an efficient heat integration process, which might also use lower grade phosphate ore and have a smaller environmental impact, there was the promise of a lower cost phosphoric acid production process making a clean, high-concentration phosphoric acid product.

Finally, in 1981, Dr. Robert Hard at ORC proposed his kiln-based process, where all of the heat would be supplied by carbon-containing feed agglomerates utilising cheap, high-sulphur, green petroleum coke. His concept was partially demonstrated in a 33-inch diameter by 30-ft long rotary pilot kiln reactor that produced high-quality phosphoric acid without problems arising from melting of the kiln burden. The process demonstrated an 87% yield in a test mode (not commercial), using unbeneficiated ore from both North Florida and Baja, Mexico to produce pure, high-concentration phosphoric acid directly from the process.

Configuration of the KPA process for Idaho ore

Phosphate reserves cover a large mountainous area in eastern Idaho and northern Utah. The phosphate matrix is in two layers,

The Improved Hard Process has several environmental advantages.

The Improved Hard Process promises to transform the economics and environmental impact of the Southern Extension to phosphate rock mining in Florida.

nominally 17 ft and 35 ft thick, near the top of mountain ridges.[16] The ore is transported by large trucks to railheads, where it is transferred to unit trains and moved to washing plants in Soda Springs and Pocatello, Idaho and Vernal, Utah. The as-mined ore is suitable for the Improved Hard Process and contains the clay necessary to act as a binder in making strong agglomerates for the process. It also has sufficiently low impurity levels to avoid melting in the kiln, and about 10% moisture. The Improved Hard Process avoids the costs necessary for wet acid plants, associated with washing the clay out of the ore and maintaining the associated waste clay storage ponds. As originally identified in Hard's patent and optimised in my recent work, readily available additional silica as a second raw material is required over that available in the currently as-mined ore to avoid the kiln burden melting problems experienced by earlier researchers of kiln-based processes. Alternatively, lower-grade phosphate ores dilute more with silica (down to 15% P_2O_5), which is suitable for the Improved Hard Process. These lower-grade phosphate resources are currently below the economic minimum for processing by the West Coast wet acid plants.

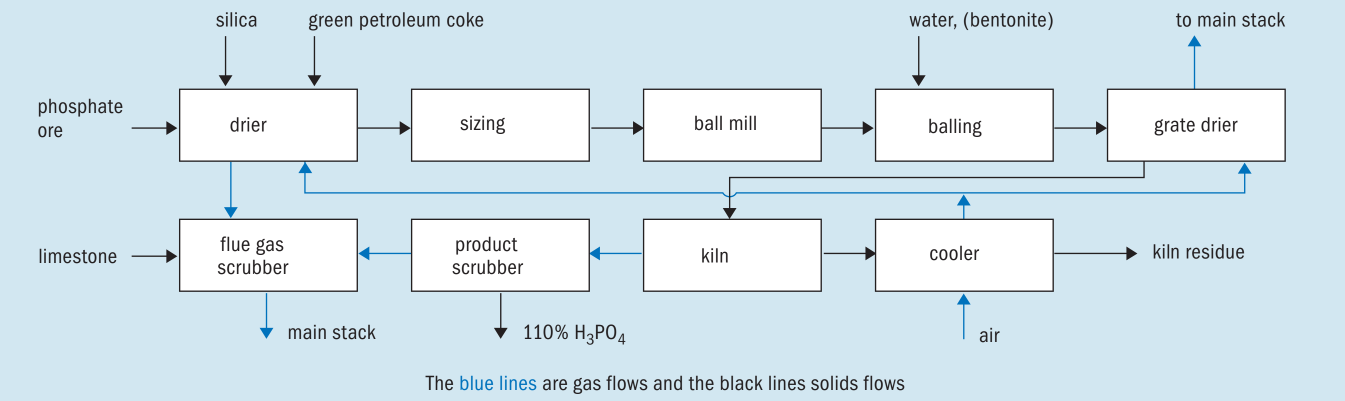
The third raw material for the Improved Hard Process is green, petroleum coke. Over 60 million s.tons of petroleum coke are available as a by-product from oil refineries worldwide. In the United States, relatively minor fractions are used as fuel in cement manufacture and blended into power plant feed. Some are used to make calcined coke for metallurgical applications. However, most of it is shipped overseas as the sulphur in the petroleum coke leads to undesirable sulphur gas emissions when used in power generation. The Improved Hard Process is a good home for high-sulphur green petroleum coke. The sulphur is mostly absorbed in the solid residue from the process (ala cement manufacture). A relatively small flue gas desulphurisation unit is required to absorb the remainder of the SO_2 emitted, as well as some silicon tetrafluoride that exits the kiln and hydrator.

The raw materials (ore with clay, silica and coke) are mixed, dried and rough-sized before being co-ground in an open circuit ball mill. The co-ground mixture is combined with a small amount of water and formed into agglomerates in a balling drum. The agglomerates are dried on a low temperature travelling grate and then fed into a countercurrent, high-temperature kiln. The phosphorus values are extracted from the kiln solids reporting to the kiln off-gas as gaseous P_4O_{10}, mixed with CO_2 and nitrogen and a modest amount of water vapour. The phosphorus oxide value, which comprises about 8% of the weight of the off-gas, is scrubbed in a hydrator of similar design to that used in the furnace acid industry to make phosphoric acid at about 76% P_2O_5 content. The hot kiln solids are cooled with air, which is then used to dry the raw materials prior to grinding and the agglomerates prior to entering the kiln. There is enough heat in the green petroleum coke to supply all of the heat requirements of the process. Only a small kiln burner is required for start-up and stability control. (Fig. 1)

Configuration of the Improved Hard Process for Florida Southern Extension and North Carolina ores

Florida and North Carolina phosphate reserves occur below the water table, with relatively high levels of associated clay. If the matrix were to be mined and transported by conveyor, truck, or rail to an Improved Hard Process facility, the clay would retain high levels of water in the mixture (e.g. 100% moisture on a dry basis). The cost of drying this matrix ore for grinding is prohibitive. A solution to this issue is

Fig 1: **Block diagram of the Improved Hard Process**



The blue lines are gas flows and the black lines solids flows

Table 1: **Raw material analysis and other data for proposed plant sites**

Florida S. Extension	CaO (%)	P_2O_5 (%)	MgO (%)	Insolubles (%)	Fraction of matrix (%)	Zone depth	Production (s.ton/acre)
Upper Zone:							
Pebble	41.8	27.8	0.52	12.0	11	Average	2,900
Float Feed	9.9	6.3	0.12	75.9	69	14 ft	
Concentrate Clay	46.6	31.9	0.43	6.5	14		3,600
	15.3	8.7	1.9	46.1	20		
Lower Zone:							
Pebble	35.8	17.0	6.19	13.9	8	Average	4,900
Float Feed	12.6	7.2	0.67	69.3	58	27 ft	
Concentrate Clay	44.8	28.6	1.21	4.8	11		6,800
	19.8	2.2	11.50	29.1	35		
Idaho:							
Raw Ore	37.3	26.15	0.51	20.34	100	-	-
Washed Ore	43.5	30.68	0.48	12.48	73.7		
N. Carolina:							
Float Feed	27.3	16.1	0.39	42.6			
Bentonite	1.8	0	1.50	66.9	-	-	-

to wash the ore as currently practised for use in wet acid plants and use the derived pebble and float feed (or some concentrate if required to sweeten the P_2O_5 level) as input to the drier. Pebble, float feed, and concentrate dewater readily to a level consistent with the availability of waste heat from the Improved Hard Process to dry the materials. After these materials are mixed with the required proportion of green petroleum coke, dried and co-ground, then an aqueous slurry of wash waste clay or bentonite is added back to the mixture to supply the moisture and clay needed to make strong agglomerates. The remainder of the process remains the same as that described for the Idaho ore.

If it is desired to use phosphate resources containing higher levels of Mg from the lower zone of the Florida Southern Extension, the amount of silica in the mixture must be increased to combine with both the extra calcium and Mg from dolomite and calcite in the ore. The kiln solids products will also contain calcium and Mg monosilicate. The use of lower zone ore results in a P level in the agglomerates charged into the kiln being marginally reduced, so the grinding costs and other processing costs are marginally increased. The higher Mg content associated with the lower zone in the Florida Southern Extension, which is not currently being mined when the upper zone is mined, could be utilised in the Improved Hard Process for the incremental cost of mining and processing it.

The yield losses and significant cost encountered in the beneficiation of wet rock concentrate for the wet acid process is avoided by the Improved Hard Process with North Carolina reserves and partially avoided with reserves from the Florida Southern Extension. Also, the phosphate value in waste clay that is used in the agglomeration process is extracted by the Improved Hard Process to form more phosphoric acid product. In the Southern Extension, the lower zone is thicker than the upper zone. It contains on average about 43% more recoverable P_2O_5 than the upper zone. The amount of phosphorus in the pebble material - particularly in the lower zone - is insufficient to bring the P content of the mixture of float feed and pebble up to a suitable P_2O_5 level for feed to the Improved Hard Process. Some additional beneficiation of the flotation feed output from ore washing is required in this case. However, both rougher and cleaner circuits of the Crago phosphate beneficiation process needed to produce rock concentrate for the wet acid process are not required for the Improved Hard Process. New approaches to flotation may be possible when less than half of the silica needs to be removed for the Improved Hard Process.

Table 1 provides the raw material analysis and other data for raw materials at each of the sites outlined above. The reserves available in the upper and lower zones of the Florida Southern Extension and their analysis were taken as the average reserve value from the Florida Institute of Phosphate Research study 02-082-105.[17] The analysis of the other raw materials was provided by our analysis of samples supplied by the companies involved, as shown in Table 1.

Cost estimates for raw materials

The cost estimate for washed West Coast rock of $29.45/s.ton f.o.b. plant was derived from data in the 2003 TFI report. After washing out the clay, West Coast rock – which is already high in P_2O_5 content – is not further beneficiated for the wet acid plants. The cost of washing the ore and maintenance of clay ponds is estimated to be 30% of the cost of the washed rock. About 14% of the matrix phosphate values are lost to the clay ponds when washing rock for use in wet acid plants. Based on these values, the cost of as-mined West Coast ore delivered to a West Coast KPA plant is estimated to be $15.20/s.ton. Silica needed for an Idaho plant is readily available from nearby surface deposits. The estimated delivered cost is $5/s.ton of silica.

The cost of mining the ore and transporting it by slurry pipeline to the beneficiation plant on the East Coast was estimated to be about 70% of the total beneficiated rock cost, including the cost of clay and tailing disposal from the beneficiation plant. Washing and beneficiation were estimated at 10% and 20% of the beneficiated rock cost respectively. It is further assumed that the beneficiation step in the Florida Southern Extension gives a 90% yield. The incremental cost of recovering

Table 2: **Improved Hard Process and WPA phosphoric acid costs**

	Cost ($/s.ton)	**t/t P_2O_5**	**Cost ($/s.ton P_2O_5)**		
Idaho:					
Raw Ore	15.20	3.98	60.55		
Silica	5.00	2.51	12.55		
Green Pet. Coke	48.00	0.69	33.08		
Production Cost KPA			54.00		
Total Idaho		**7.18**	**160.17**		
North Carolina:					
Float Feed	11.16	6.47	72.20		
Silica	5.00	1.16	5.82		
Bentonite	110.00	0.05	5.91		
Green Pet Coke	32.00	0.69	22.05		
Production Cost KPA			62.98		
Total N Carolina		**8.38**	**168.96**		
Florida Southern Extension:	**Upper Zone Raw Materials**			**Lower Zone Raw Materials**	
				t/t P_2O_5	**Cost ($/s.ton P_2O_5)**
Pebble Upper Zone	21.33	1.56	33.27		
Pebble Lower Zone	3.20			1.51	4.83
Float Feed, Upper Zone	4.83	4.13	19.95		
Float Feed, Lower Zone	1.35			5.96	8.04
Concentration, Upper Zone	34.93	1.00	34.93		
Concentration, Lower Zone	18.89			1.13	21.29
Clay, Upper Zone	5.00	0.34	1.70	0.39	1.96
Green Pet Coke	26.00	0.69	17.94	0.69	17.91
Production Cost KPA			58.05		81.64
Total Florida S. Extension		**7.72**	**165.84**	**10.86**	**135.67**
Wet Acid Process:					
Beneficiated ore	29.48	3.60	105.90		
Sulphuric acid	21.06	2.74	57.64		
Production Cost (WPA)			42.00		
WPA to SPA	60		60.00		
Total Wet Process Acid		**6.34**	**265.54**		

the phosphate values in the lower zone of the Southern Extension is further reduced, as the mine development and overburden removal costs have already been sunk to remove the upper zone and the slurry pipeline is in place. The slurry pipeline length for this analysis is 4 miles. The incremental mining costs for the lower zone of the Southern Extension were derived from 2001 mining cost data. The weighted average of the cost of the Improved Hard Process for the Upper Zone, which has full mining and beneficiating costs and Lower Zone, which has only the incremental costs, will provide the Improved Hard Process cost when used for the full mine output.

High-sulphur petroleum coke in much larger quantities than required for a mature Improved Hard Process industry is currently shipped from oil refineries, many of them surrounding the Gulf of Mexico, to foreign markets. A delivered 2004 cost for a Southern Extension KPA plant is $26/s.ton and $32/s.ton for a North Carolina Improved Hard Process plant. Because no refineries are close to the Idaho phosphate deposits, the delivery of high-sulphur petroleum coke is higher, resulting in an estimated delivered price of $48/s.ton.

The proportions of raw materials to optimise the silica and reductant level at each site are combined with the cost of raw materials and production cost analysis from the 2004 JDC engineering study with the results shown in Table 2. Also shown in Table 2 is the average cost for making wet process phosphoric acid as provided by the 2003 TFI study for making black acid. An estimate of $60/s.ton as the cost of converting black acid (nominally 26% P_2O_5) to SPA (76% P_2O_5) is also provided.

This cost varies widely, depending on the phosphate rock used in the wet acid process, and includes the evaporation requirement, with a yield loss associated with removing Mg-contaminated sludge and preparing the phosphate ore to remove organics. The phosphoric acid produced in Florida contains so much Mg impurity that none is converted to SPA. In this case, KPA would enable a product with growing market demand to be economically produced where it is not economically practical to do so now.

Improved Hard Process acid quality

In general, the quality of acid produced by the KPA process is similar to the quality from the furnace acid process, which uses the same chemistry to produce P_4O_{10} (g) in an off-gas stream, and the same general hydrator equipment to scrub it into a high-strength acid.

As long as the amount of water vapor in the kiln off-gas is sufficiently low, the acid strength of 76% P_2O_5 is readily obtained. Elements like Ca, Mg and Al that are not reduced in the kiln burden are not transferred to the kiln off-gas except by dust entrainment.

The main contaminates to the acid product not found in furnace acid are Na and K. About 15% volatilises to the kiln off-gases and transfers to the acid product. Like the furnace acid process, some of the small quantity elements reduce and form volatile metals which do transfer to the acid product. These elements are zinc, cadmium, arsenic, and mercury. Should the KPA process have 96% phosphorus yield to the acid product with all of the Zn, Cd, Ar and mercury found in the ore transferring quantitatively to the product, and 15% of both the sodium and potassium transferring to the acid product, then the projected analysis of the KPA acid product for the various ore sources is shown in Table 3. The acid produced by KPA also contains ppm amounts of iron, chromium, and nickel, which arise from the slow but finite attack of the product acid on the wall of the hydrator system.

Table 3: **Calculation of acid quality**

Element	Idaho	North Carolina	Florida
P_2O_5 (%)	76	76	76
K (%)	0.3	0.1	0.1
Na (%)	0.2	0.5	0.3
Ca (ppm)	214	128	45
Hg (ppb)	1,070	172	n/a
Zn (ppm)	3,477	983	180
As (ppm)	43	74	84

Discussion and conclusion

Several advantages can be attributed to the Improved Hard Process. It utilises resources that are unsuitable or difficult to process by the wet acid methods. High-silica phosphate deposits, phosphate deposits that contain higher levels of Mg impurity, phosphate deposits that contain higher levels of organic materials or deposits containing combinations of these impurities are all potential raw materials sources for the Improved Hard Process.

The Improved Hard Process also has several environmental advantages. Regardless of the ore used, the process produces solid waste in the form of amorphous agglomerates suitable for aggregate uses rather than gypsum piles. The glassy, amorphous nature of the spent agglomerates seals in impurities. These agglomerates readily pass the Toxicity Characteristic Leaching Procedure (TCLP) tests for land disposal. With favourable ores (such as those from Idaho), there are no clay storage ponds or flotation plant tailings.

The Improved Hard Process is a dry process, so threats to ground or surface waters are reduced. It also makes use of green, high-sulphur petroleum coke, an energy resource produced by the United States but shipped to foreign countries. Improved Hard Process phosphoric acid is produced as a relatively pure, high-concentration acid suitable for use in liquid fertilizers.

Liquid fertilizers have enjoyed increasing markets at the expense of solid fertilizers over the last 40 years. When the P requirement of a crop is well characterised over the crop growth cycle, matching liquid fertilizer applications to that growth cycle can provide a more efficient transfer of the fertilizer values to the plant. As the world requires more efficient processes for leaner phosphate resources to produce higher quality and more efficient products and ever-greater environmental stewardship, the time has come to complete the commercial development of the KPA process. ■

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